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The Applicability Of Activities In Kinetic Expressions: a More Fundamental Approach To Represent the Kinetics Of the System CO₂-OH- In Terms Of Activities

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The Applicability Of Activities In Kinetic Expressions: a More Fundamental Approach To Represent the Kinetics Of the System CO₂-OH- In Terms Of Activities

Jens Haubrock, J. A. Hogendoorn, and Geert F. Versteeg

Abstract

In this paper the applicability of using activities instead of concentrations in kinetic expressions has been investigated using the reaction of CO₂ with various hydroxide solutions as a model system. For this system it is known that when the reaction rate constant is based on the use of concentrations in the kinetic expression, this “constant” depends both on the counter ion in the solution and the ionic strength. Using the data of Pohorecki, it could be revealed that the use of activities reduces the influence of the ionic strength on the derived rate constant to a very large extent. Hence the kinetic constant using the activity based approach seems much more like a real constant than the “constant” using the traditional kinetic expression using concentrations. Besides this, the absolute values of the rate constants for the three different counter-ions also moved closely together. This points out that applying one fixed rate constant, independent of the counter-ion or the ionic strength, might be sufficient for describing the reaction rate in the studied system. A large advantage of using activities in kinetic expressions is that the fundamental description of kinetics and thermodynamics is consistent which each other so that at equilibrium the net reaction rate (based on the kinetic expression) is indeed zero.

KEYWORDS: activities, kinetics, CO₂, VLE, Pitzer

1 INTRODUCTION

The kinetics of CO_2 -absorption in caustic solutions, especially in sodium hydroxide, have been extensively studied within the last decades. In these studies it has been found that the reaction rate constant is not only dependent on the concentrations of the reacting species, but also affected by the ionic strength of the caustic solution and the nature of the cations present in the hydroxide solution (Pohorecki and Moniuk, 1988; Kucka et al., 2002; Nijssing et al., 1959). The following two reactions are known to take place:

1. $\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$
2. $\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$

The rate of reaction 2 is significantly higher than that of reaction 1, thus reaction 1 is rate determining for the overall reaction rate.

In literature, the kinetics of reaction 1 are typically described using an irreversible-second-order reaction ($r = k_1 \cdot c_{\text{CO}_2} \cdot c_{\text{NaOH}}$), where all possible effects of non-idealities are lumped in the reaction rate constant k_1 (Pohorecki and Moniuk, 1988; Kucka et al., 2002). This approach is sufficient to represent the experimental data of a single specific study but lacks the fundamental character of the reaction rate constant only being a function of temperature.

In this work it is attempted to derive a rate expression for the absorption of CO_2 based on the activities of the species, and not on the commonly used concentrations. Recently, the use of activities in kinetic expressions has proven to reflect the experimental results much better than the concentration based approach (Rehfinger and Hoffmann, 1990). This holds especially for highly non-ideal systems, where both polar and apolar components are involved (Poepken et al., 2000).

The use of activities in kinetic expressions also has the additional advantage that now equilibrium (typically expressed using activities) and kinetics seem to be more easily compatible. Especially in processes like reactive distillation where also phase equilibria play a significant role, this seems to be a major advantage (Venimadhavan et al., 1999).

In the present study, the results of determining the activity coefficients for the system $\text{CO}_2\text{-OH}^-$ with the Pitzer-model (Pitzer, 1973) and the representation of the kinetics incorporating these activity coefficients will be presented. The newly developed kinetic expression will be compared to those available in literature.

2 THERMODYNAMIC MODEL

2.1 Modelling

In this section the thermodynamic model used in the interpretation of the kinetic studies will be described. In the vapor-liquid equilibrium of the system $\text{CO}_2 - \text{NaOH} - \text{H}_2\text{O}$ it has been assumed that the only species present in the gas phase, are CO_2 and H_2O . Furthermore it will be supposed that the dissolved NaOH is entirely dissociated, thus the possibility of a solid-liquid equilibrium can be disregarded. In Figure 1 a schematic drawing of the system is presented. The only components existing in the gas phase are H_2O and CO_2 respectively. In the liquid phase CO_2 , H_2O , OH^- and the products of the chemical reactions as depicted in Figure 1 are present.

For the description of the chemical reactions the temperature dependent equilibrium constants of the following reactions are taken into account:



In the liquid phase the condition for equilibrium as defined according to Rumpf et al. (Rumpf et al., 1998) is used:

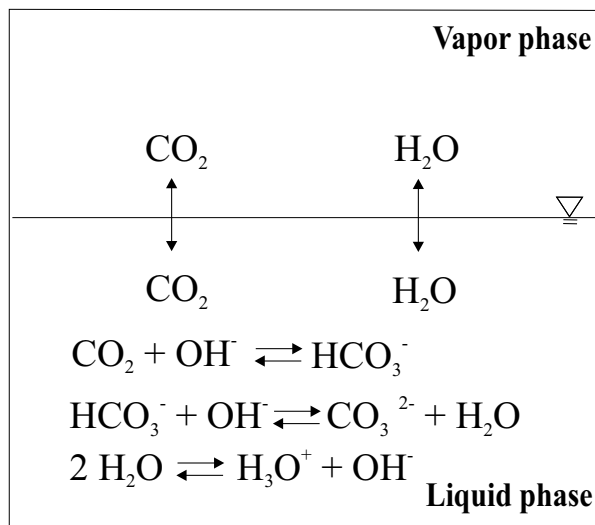


Figure 1. VLE and chemical reactions in the system $CO_2 - NaOH - H_2O$

$$K_j^{EQ} = \prod_{i=1}^3 (a_i^{\nu_{i,EQ}}) = \prod_{i=1}^3 (\gamma_i \cdot m_i)^{\nu_{i,EQ}} \quad (4)$$

The equilibrium constants for the reactions (1)-(3) together with the material balances for carbon and hydrogen as well as an electro-neutrality balance allow the calculation of the amounts of each species in the liquid phase. Activity coefficients in the equilibrium equations are introduced to take the non-ideality of the liquid phase into account. The material balances applied in this model are as follows:

$$\text{Carbon - balance :} \quad n_{CO_2}^0 = n_{CO_2} + n_{HCO_3^-} + n_{CO_3^{2-}} \quad (5)$$

$$\text{Hydrogen - balance :} \quad 2 \cdot n_{H_2O}^0 + n_{OH^-}^0 = 2 \cdot n_{H_2O} + n_{OH^-} + n_{HCO_3^-} + 3 \cdot n_{H_3O^+} \quad (6)$$

The electro-neutrality balance gives:

$$n_{OH^-} + n_{HCO_3^-} + 2 \cdot n_{CO_3^{2-}} - n_{H_3O^+} - n_{Na^+} = 0 \quad (7)$$

The phase equilibrium for water and carbon dioxide is described with the subsequent equations:

$$p \cdot y_w \cdot \phi_w'' = p_w^s \cdot \phi_w^s \cdot a_w \cdot \exp\left(\frac{v_w \cdot (p - p_w^s)}{R \cdot T}\right) \quad (8)$$

$$p \cdot y_i \cdot \phi_i'' = H_{i,w}^m(T, p_w^s) \cdot m_i \cdot \gamma_i^* \exp\left(\frac{v_{i,w}^\infty \cdot (p - p_w^s)}{R \cdot T}\right) \quad (9)$$

As it can be seen from the above listed equations the model requires the knowledge of a number of parameters like the equilibrium constants K_1 to K_3 , the activities γ_i^* of all species in the liquid phase, Henry's constant for carbon dioxide dissolved in pure water ($H_{CO_2,w}^m$), the vapor pressure (p_w^s) and the molar volume (v_w) of pure water, the partial molar volume ($v_{CO_2,w}^\infty$) of carbon dioxide, as well as information on the fugacity coefficients ϕ_i'' in the gas phase.

Table 1. Equilibrium constants for chemical reactions

$$\ln K_R = A_R / (T[K]) + B_R \ln(T[K]) + C_R(T[K]) + D_R$$

| Equ. constant | A | B | C | D | Reference |
|-----------------------------|----------|----------|------------|----------|---------------------------------|
| K ₁ (reaction 1) | 5719.89 | 7.97117 | -0.0279842 | -38.6565 | Kawazuishi and Prausnitz (1987) |
| K ₂ (reaction 2) | 4308.64 | 4.36538 | -0.0224562 | -24.1949 | Kawazuishi and Prausnitz (1987) |
| K _w (reaction 3) | -13445.9 | -22.4773 | 0 | 140.932 | Edwards et al. (1978) |

Table 2. Henry's constant for the solubility of carbon dioxide in pure water

$$\ln H_{CO_2,w} [MPa \cdot kg \cdot mol^{-1}] = A_{CO_2,w} + B_{CO_2,w}/T[K] + C_{CO_2,w}(T[K]) + D_{CO_2,w} \ln(T[K])$$

| Henry-constant constant | A _{CO_{2,w}} | B _{CO_{2,w}} | C _{CO_{2,w}} | D _{CO_{2,w}} | Reference |
|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------|
| H _{CO_{2,w}} | 192.876 | -9624.4 | 0.01441 | -28.749 | Rumpf and Maurer (1993) |

The temperature dependent equilibrium constant for water was taken from Edwards et al. (1978) whereas the equilibrium constants for the other two reactions have been taken from Kawazuishi and Prausnitz (1987) (see Table 1). Henry's constant for the solubility of CO₂ in water was taken from Rumpf and Maurer (1993) (see Table 2). Saul and Wagner (1987) provided the equations for the vapor pressure and the molar volume of pure water. The fugacity coefficients were calculated with the virial equation of state truncated after the second virial coefficient. The second virial coefficients of water and carbon dioxide were calculated from correlations based on data suggested by Dymond and Smith (1980) (see Table 3). The mixed virial coefficient $B_{CO_2,w}$ was taken from Hayden and O'Connell (1975) (see Table 4). The partial molar volume of carbon dioxide dissolved in water at infinite dilution $v_{CO_2,w}^\infty$ was calculated according to the method of Brelvi and O'Connell (1972) (see Table 4).

The activity coefficients in the liquid phase were calculated with Pitzer's equation for the Gibbs energy of an electrolyte solution (Pitzer, 1973). The semi-empirical Pitzer model has been successfully applied by a number of authors e.g. Beutier and Renon (1978), Engel (1994), Rumpf et al. (1998) and van der Stegen et al. (1999) for different electrolyte system. In the extended Pitzer equation, which is described in more detail in the appendix, the ion-ion binary interaction parameters $\beta_{i,j}^{(0)}$ and $\beta_{i,j}^{(1)}$ as well as the ternary interaction parameter $\tau_{i,j,k}$ are characteristic for each aqueous single electrolyte solution. These parameters are solely determined by the properties of the pure electrolytes.

Table 3. Pure component second virial coefficients ($273 \leq T[K] \leq 473$)

$$B_{i,i} [cm^3 \cdot mol^{-1}] = a_{i,i} + b_{i,i} \cdot (c_{i,i}/T[K])^{(d_{i,i})}$$

| i | a _{i,i} | b _{i,i} | c _{i,i} | d _{i,i} | Ref. |
|------------------|------------------|------------------|------------------|------------------|-------------------------|
| CO ₂ | 65.703 | -184.854 | 304.16 | 1.4 | Dymond and Smith (1980) |
| H ₂ O | -53.53 | -39.29 | 647.3 | 4.3 | Dymond and Smith (1980) |

Interactions between ions and neutral molecules can also be considered in the extended Pitzer model which is important for systems where neutral molecules are dissolved in electrolyte solutions as e.g. CO₂ in caustic solutions. A shortcoming of the Pitzer model is that its application is restricted to the solvent water (Pitzer, 1991). However, in the present study this is not a limitation as attention is focused on the CO₂-NaOH-H₂O system. An outstanding property of Pitzer's model is the ability to predict the activity

coefficients in complex electrolyte solutions from data in simple ones (Horvath, 1985). This avoids the use of triple or quadruple interaction parameters which are very scarcely reported in the open literature whereas for the most common single electrolytes binary interaction parameters are readily available.

Table 4. Mixed second virial coefficients and partial molar volumes

| T[K] | $B_{CO_2, w}$ | Ref. | $v_{CO_2, w}^\infty$ | Ref. |
|--------|--------------------------------------|-----------------------------|--------------------------------------|-----------------------------|
| | [cm ³ mol ⁻¹] | | [cm ³ mol ⁻¹] | |
| 313.15 | -163.1 | Hayden and O'Connell (1975) | 33.4 | Brelvi and O'Connell (1972) |
| 333.15 | -144.6 | Hayden and O'Connell (1975) | 34.7 | Brelvi and O'Connell (1972) |
| 353.15 | -115.7 | Hayden and O'Connell (1975) | 38.3 | Brelvi and O'Connell (1972) |
| 373.15 | -104.3 | Hayden and O'Connell (1975) | 40.8 | Brelvi and O'Connell (1972) |
| 393.15 | -94.3 | Hayden and O'Connell (1975) | 43.8 | Brelvi and O'Connell (1972) |
| 413.15 | -85.5 | Hayden and O'Connell (1975) | 47.5 | Brelvi and O'Connell (1972) |

In the liquid phase the reactions 1, 2 and 3 as depicted in Figure 1 take place. For the computation of the equilibrium constants the activity coefficients of the following species were evaluated with the Pitzer model: CO_2^l , OH^- , HCO_3^- , CO_3^{2-} and H_3O^+ .

For a sodium hydroxide- CO_2 solution the interaction parameters used in Pitzer's model can be divided into three groups:

1. Parameters describing interactions between neutral solutes: The only neutral solute is CO_2 which has only a very low solubility in water. Thus all binary and ternary interactions of CO_2 have been set to zero.
2. Parameters describing interactions between charged species: For the system sodium hydroxide-water the interaction parameters have been taken from Pitzer and Peiper (1982). On the basis of expected relative concentrations of the various components in the solution, the ion-ion interactions listed in Table 5 are expected to be significant. These interaction parameters have been incorporated as the ions or molecules will be present in high concentrations in the solution. It is anticipated that the interactions between these species account to a large extent for the non-idealities in the solution.
3. Parameters describing interactions between the neutral solute carbon dioxide and charged species. For the interaction parameters between carbon dioxide and sodium ions the parameter from Rumpf and Maurer (1993) was used. Interactions between carbon dioxide and dissolved bicarbonate or carbonate have been omitted as those interactions are reported to be negligible (Edwards et al. (1978) and Pawlikowski et al. (1982)). Due to the low concentration H_3O^+ ions in the solution, all interaction parameters between this component and CO_2 have been set to zero. Furthermore the interaction parameters between OH^- ions and CO_2 molecules have been set to zero as not the hydroxide ions effect the reaction rate but the nature of the counter-ions introduced by the hydroxide solution.

For a better overview all interactions which have been taken into account in the present $CO_2 - NaOH - H_2O$ model are listed in Table 5. For the two other model systems studied in this work, namely $CO_2 - KOH - H_2O$ and $CO_2 - LiOH - H_2O$, only the interactions in Pitzer's activity model have to be altered in the equilibrium model. The required interactions for these systems as used in this study can be found in Table 6. All needed interaction parameters for the considered systems are known which avoids cumbersome fitting to scarcely available experimental data.

The effect of temperature on the interaction parameters has been neglected. This corresponds with

the assumption that the temperature effect on the activity coefficient is the same for each component (Engel, 1994). The dielectric constant of pure water used in the Pitzer model was taken from Horvath (1985).

Table 5. Considered ion-ion interaction parameters in the CO₂, NaOH, H₂O system at 25° C

| Interaction | $10^2 \cdot (\beta^0, \lambda)$ (kg/mol) | $10 \cdot \beta^1$ (kg/mol) | $10^3 \cdot C^\phi$ (kg ² /mol ²) | Ref. |
|---|---|--------------------------------|---|---------------------------|
| Na ⁺ - OH ⁻ | + 8.64 | + 2.53 | + 4.40 | (Pitzer and Peiper, 1982) |
| Na ⁺ - HCO ₃ ⁻ | + 2.80 | + 0.44 | 0 | (Pitzer and Peiper, 1982) |
| Na ⁺ - CO ₃ ²⁻ | + 3.62 | + 15.1 | + 5.2 | (Pitzer and Peiper, 1982) |
| CO ₂ - Na ⁺ | + 12.8 | - | - | (Pitzer and Peiper, 1982) |

Table 6. Considered ion-ion interaction parameters in the CO₂, KOH, H₂O and CO₂, LiOH, H₂O system at 25° C

| Interaction | $10^2 \cdot (\beta^0, \lambda)$ (kg/mol) | $10 \cdot \beta^1$ (kg/mol) | $10^3 \cdot C^\phi$ (kg ² /mol ²) | Ref. |
|---|---|--------------------------------|---|--------------------|
| K ⁺ - OH ⁻ | + 12.98 | + 3.20 | + 4.1 | Roy et al. (1984) |
| K ⁺ - HCO ₃ ⁻ | - 1.07 | + 0.48 | 0 | Roy et al. (1984) |
| K ⁺ - CO ₃ ²⁻ | + 12.88 | + 14.33 | + 0.5 | Roy et al. (1987) |
| CO ₂ - K ⁺ | + 9.46 | | | Engel (1994) |
| Li ⁺ - OH ⁻ | + 1.5 | 1.4 | - | Roy et al. (1987) |
| Li ⁺ - HCO ₃ ⁻ | no | data | available | |
| Li ⁺ - CO ₃ ²⁻ | - 38.934 | - 22.737 | - 162.859 | Deng et al. (2002) |
| CO ₂ - Li ⁺ | + 5.8 | - | - | Schumpe (1993) |

2.2 Experimental results vs. model

The model predictions have been compared to experimental values taken from Rumpf et al. (1998). Upon this comparison it can be concluded that the model can predict the experimental equilibrium values accurately for m_{CO_2}/m_{OH^-} ratios larger than 1 up to m_{CO_2}/m_{OH^-} ratios of 1.5. In this range the relative error with respect to the experimental data is less than 6%.

Nevertheless the model shows a deviation from experimentally obtained pressures for m_{CO_2}/m_{OH^-} ratios lower than 1. Here the relative error can amount up to 43% (see Figure 3). In itself this is not necessarily a problem, as the goal of the equilibrium model in this study is the prediction of activity coefficients and not of VLE data. The comparison between experimental values and model prediction is illustrated in Figure 2 and 3, respectively.

In Figure 2 the predicted and experimentally obtained results for a fixed temperature of 313 K and a fixed molality of NaOH= $0.9613 \frac{mol}{kg}$ are displayed. Apart from the value left-most, the relative error is below 5 percent for these conditions. The leftmost point exhibits a relative error of 34 percent.

Furthermore experimental and predicted results for a fixed molality of NaOH= $1.0441 \frac{mol}{kg}$ and a fixed temperature of 353 K have been compared in Figure 3. For ratios of m_{CO_2}/m_{OH^-} less than 1 the

relative error can amount up to 43 %. This emphasizes the fact that the model predictions differ from the available experimental data for m_{CO_2}/m_{OH^-} ratios equal or less than 1. In the CO_2 molality range from 1.2 to 1.4 the computed and experimental values differ less than 6 percent. The utmost right point has a deviation of 16 percent.

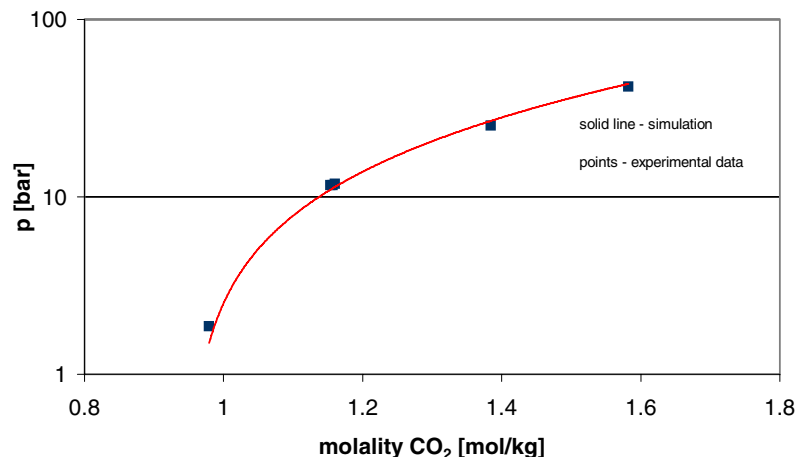


Figure 2. Comparison experimental results vs. model at 313K

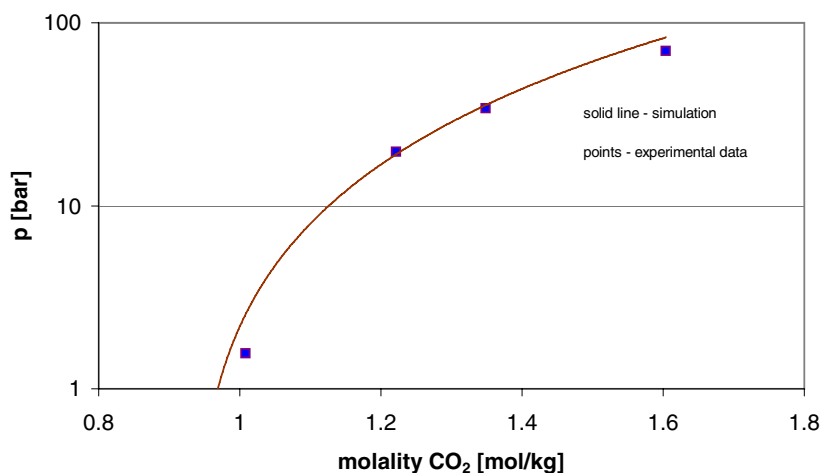


Figure 3. Comparison experimental results vs. model at 353K

The variations between the model predictions and the experimental results are most pronounced for ratios of m_{CO_2}/m_{OH^-} less than 1 where, especially at very low loadings, the total pressure (water vapor pressure and partial pressure of CO_2) is nearly not affected by the addition of carbon dioxide. In that low pressure range (0-0.9 bar), the absolute uncertainty in the total pressure readings in the experiment can reach up to 5 % according to Rumpf et al. (1998). This signifies that the deviation between model and experiments in the low pressure regime may partially be attributed to the experimental uncertainty in the measured data points. The thermodynamic model predicts experimental results with an error of 6 % if excluding low pressure values, however, the deviation at low loadings (low pressures) can be significant.

The deviation in the low pressure range (0-0.9 bar) between experimental and calculated values can be severe but it can be concluded from the above said that it is not sure whether this is because the model exhibits a possible weakness in this regime or the experimental results are not accurate enough. As absorption experiments are often carried out in this regime, the activity related parameters as used in this

study for the evaluation of the experiments in this regime should be reliable. This means that for the purpose of this study mainly the values of the activity coefficients are of importance and not the absolute pressures predicted by the VLE model.

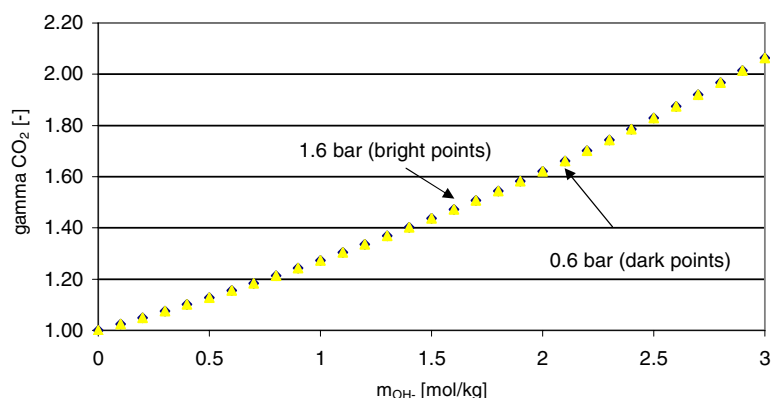


Figure 4. Activity coefficients of CO_2 as a function of the hydroxide molality for two pressures

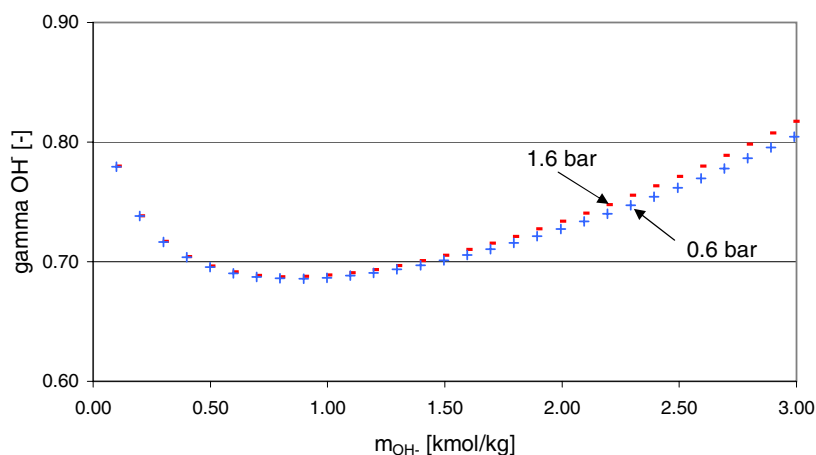


Figure 5. Activity coefficients of OH^- as a function of the hydroxide molality for two pressures

In Figure 4 the activity coefficients for CO_2 in a sodium hydroxide solution are shown as a function of the OH^- -molality for two different pressures. Furthermore the activity coefficients of OH^- as a function of the OH^- -molality for two different pressures are presented in Figure 5. As can be seen the absolute values of the activity coefficients are nearly not affected by the absolute pressure. Thus the thermodynamic model meets the purpose to yield reliable activity coefficients for the system of interest and according to this will be applied in the kinetic studies presented in the following section.

3 REVIEW ON THE KINETICS FOR THE SYSTEM CO_2 - OH^-

Several authors have already measured the kinetics for the reactions which occur during the absorption of CO_2 into aqueous solutions of hydroxides (Pohorecki and Moniuk, 1988). The following reactions are taking

place:



The physical absorption of gaseous carbon dioxide in water is described by equation 10. This is a comparatively fast process, thus equilibrium at the gas-liquid interface, described by Henry's law, can be assumed (Pohorecki and Moniuk, 1988). The reaction of CO_2 with water can be neglected as its rate of reaction is 30 times slower than that of reaction 11 for $pH > 10$ (Danckwerts, 1970). This condition is fulfilled for all caustic solutions in this study.

According to Hikita and Asai (1976) and Pinsent et al. (1956) reaction 12 is a proton transfer reaction which proceeds at a much higher speed than reaction 11. Therefore reaction 12 is treated as an instantaneous reversible reaction. Reaction 11 is much slower than reaction 12 and its equilibrium constant of $4.4 \times 10^7 \text{ kg/mol}$ at 298 K (Kawazuishi and Prausnitz, 1987) indicates that it is practically irreversible. The assumption of irreversibility of reaction 11 is justified at low loadings of CO_2 (Danckwerts, 1970). Pohorecki measured absorption rates at a reduced pressure of 0.3 bar with pure CO_2 in the gas phase. Thus the CO_2 loading in the liquid phase is low and reaction 11 can indeed be treated as an irreversible reaction. Besides that reaction 11 is the rate determining reaction of the three occurring reactions.

In literature (e.g. Pohorecki and Moniuk (1988) and Nijssing et al. (1959)) the kinetic expression of CO_2 with hydroxide ions is mostly described based on an irreversible reaction:

$$r = k_{OH^-} \cdot c_{OH^-} \cdot c_{CO_2} \quad (13)$$

Absorption rate experiments have been performed among others by Nijssing et al. (1959), Roberts and Danckwerts (1962), Himmelblau and Babb (1958), Sirs (1958a), Sirs (1958b), Pinsent et al. (1956), Hikita and Asai (1976), Pohorecki and Moniuk (1988) and Kucka et al. (2002) to determine the value of the reaction rate constant k_{OH^-} in equation 13.

Some authors measured the reaction rate constant only in dilute solutions and extrapolated their results to infinite dilution solely for identifying the rate constant $k_{OH^-}^\infty$. Other authors extended their measurements to more concentrated solutions and fitted their experimental results to an ionic strength dependent rate constant. These authors generally applied the function

$$k_{OH^-} = k_{OH^-}^\infty(T) \cdot 10^{(a \cdot I^2 + b \cdot I)} \quad (14)$$

to fit the experimental results.

4 EVALUATION OF THE KINETIC DATA IN THE OPEN LITERATURE

In the following section the results of the different authors are assessed concerning accuracy and reliability. One group of authors performed absorption experiments and extrapolated their results to infinite dilution for determining the reaction rate constant $k_{OH^-}^\infty$. In other papers (Pohorecki and Moniuk (1988), Nijssing et al. (1959) and Kucka et al. (2002)) the influence of the different cations on the reaction rate constant was examined additionally. This was done by employing three different caustic solutions, namely LiOH, NaOH and KOH, and measuring the kinetics in these solutions.

The reaction rate constant k_{OH^-} in aqueous sodium hydroxide solutions as a function of the ionic strength I , as represented in literature, is depicted in Figure 6. The reaction rate constant at infinite dilution $k_{OH^-}^\infty$ as reported by different authors is itemized in Table 7.

As can be seen from Table 7 the values for the kinetic constant at infinite dilution are in the same order of magnitude with exception of the value reported by Himmelblau and Babb (1958). This value is by a factor of 50 larger versus the others and thus can be considered being questionable. Even if the value reported by Himmelblau is excluded, the differences between the results obtained by different authors at an ionic strength > 0 are still significant (see Figure 6).

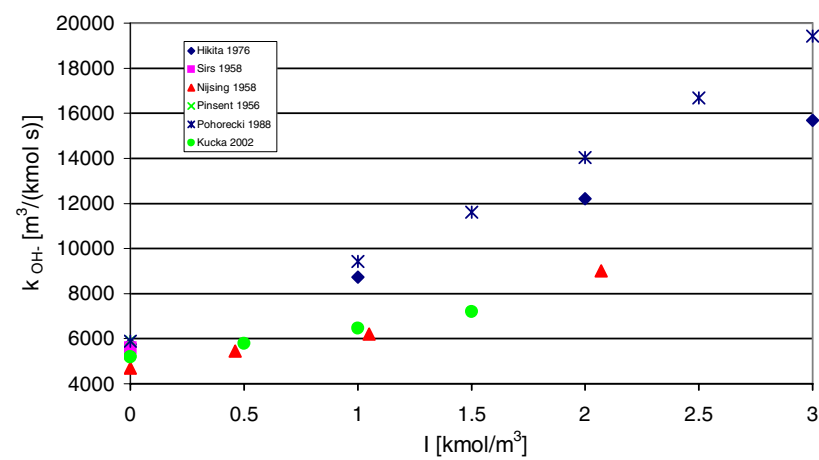


Figure 6. Dependence of k_{OH-} on I for reaction 11 at 298 K

Table 7. k_{OH-}^{∞} for infinite dilution at 293 K

| k_{OH-}^{∞} [$m^3/(kmol s)$] | Reference |
|---------------------------------------|--|
| 277000 | Himmelblau et al. Himmelblau and Babb (1958) |
| 5900 | Pinsent et al. Pinsent et al. (1956) |
| 5881 | Pohorecki et al. Pohorecki and Moniuk (1988) |
| 5748 | Hikita et al. Hikita and Asai (1976) |
| 5590 | Sirs et al. Sirs (1958a) |
| 5196 | Kucka et al. Kucka et al. (2002) |
| 4700 | Nysing et al. Nijssing et al. (1959) |

For selecting the most reliable data, the different studies have been examined concerning 1) the method of measuring the reaction rate on the one hand and 2) the assumptions and their validity for interpreting the experimental results.

1) The experimental methods used by Pohorecki and Moniuk (1988), Hikita and Asai (1976) and Nijssing et al. (1959) seem to be sound as they use well established techniques. These techniques are commonly used for absorption experiments and known to give accurate and reproducible results (Danckwerts, 1970). Pinsent et al. (1956) and Sirs (1958a) applied the rapid thermal method which is only applicable for diluted systems (Sirs, 1958a).

The highest molarity of the sodium hydroxide solution applied by these authors was 0.05 kmol/m³, thus their results can still be considered being reliable. Unfortunately, the latter two publications cannot provide information on the behavior of the rate constant at higher ionic strength which reduces their value to a certain extent.

Kucka et al. (2002) used a stirred cell reactor to carry out absorption rate experiments. This model contactor is also generally considered to be well suited for performing kinetic experiments (van Swaaij and Versteeg, 1992). Kucka measured the kinetics in sodium hydroxide solutions up to an ionic strength of 1.25 kmol/m³ and in potassium hydroxide solutions up to an ionic strengths of 0.85 kmol/m³.

2) The mass transfer models used to extract the reaction rate constant from the flux experiments have been

examined. Most authors have chosen their reaction conditions to conform to the assumption of a pseudo-first-order reaction regime. Working in the pseudo-first-order regime allows to apply an approximate analytic solution to the flux equations. Reactions of pseudo-first-order have to fulfill the subsequent two conditions:

1. $Ha > 2$
2. $E_{\infty}/Ha > \sim 5$

The Hatta-number for a pseudo-first-order reaction is defined by (Hikita and Asai, 1976):

$$Ha = \frac{\sqrt{k_1 \cdot D_{CO_2}}}{k_L} \quad (15)$$

with k_1 being the overall pseudo-first-order reaction rate constant which reads as follows:

$$k_1 = k_{OH^-} \cdot c_{OH^-} \quad (16)$$

The enhancement factor for instantaneous, irreversible reactions in terms of the film theory is expressed as follows (Baerns et al., 1992):

$$E_{\infty} = 1 + \frac{D_{OH^-} \cdot c_{OH^-}}{D_{CO_2} \cdot c_{CO_2}^{interface}} \quad (17)$$

If the experimental conditions are chosen to obey the two relations, an approximate analytical solution can be applied to interpret the experiments which facilitates the calculation of the rate constant.

The two above noted criteria have been checked for the experimental conditions reported in the different papers. In all cases the assumption of an irreversible pseudo-first order reaction could be affirmed.

Upon the assessment of the literature data using the two criteria above, it seems reasonable to take the experimental findings of Pohorecki et al., Hikita et al., Nysing et al. and Kucka et al. and to interpret them with the new approach. Since only Pohorecki et al. and Nysing et al. did experiments with sodium, potassium and lithium hydroxide solutions, the comparison of the new approach in activities is restricted to the data of these two authors.

Of these two authors only the data by Pohorecki and Moniuk (1988) have been used for a comparison because the value for the rate constant for NaOH at infinite dilution presented by Nijssing et al. (1959) deviates by almost 20 % from the values given by the other authors.

5 COMPARISON: NEW KINETIC APPROACH WITH ACTIVITIES VS. LITERATURE DATA

In this section the results of the comparison between the literature data obtained using the traditional kinetic expression from Pohorecki and Moniuk (1988) and the new approach of presenting the kinetics in terms of activities are pointed out. It is evaluated if there is indeed the need to formulate the kinetics for the system CO_2 and hydroxide ions, stemming from different caustic solutions, in the following manner:

$$r = k_{OH^-}^{\infty} \cdot \gamma_{CO_2} c_{CO_2} \cdot \gamma_{OH^-} c_{OH^-} \quad (18)$$

instead of using the traditional approach which reads as follows:

$$r = k_{OH^-} \cdot c_{CO_2} \cdot c_{OH^-} \quad (19)$$

From a fundamental point of view the rate constant k_{OH^-} should only be a function of temperature, usually in the form of an Arrhenius type expression. Nevertheless in literature the rate constant k_{OH^-} has been corrected for the non-ideal behavior of the system or better it has been fitted as a function of temperature and ionic strength as shown in equation 14. This in fact means that all possible effects of non-idealities are lumped in the kinetic constant. In the new attempt (using Eqn. 18) this has been avoided by introducing liquid phase activities to account for non-idealities. Hence the traditional lumped kinetic constant k_{OH^-} is set equal to the product of $k_{OH^-}^{\infty} \gamma_{CO_2} \gamma_{OH^-}$.

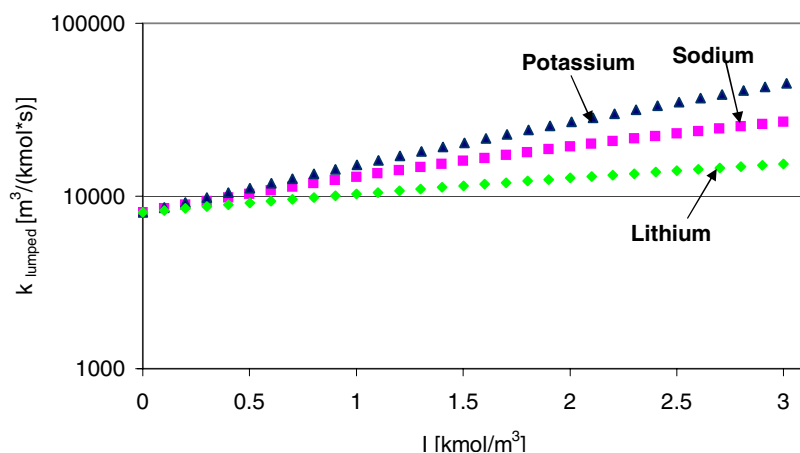


Figure 7. Traditional kinetic approach after Pohorecki and Moniuk (1988)

In Figure 7 the kinetic constants for the three caustic solutions, namely lithium, potassium and sodium are presented in the traditional way. Obviously the curves diverge from each other with increasing ionic strength which indicates that the counter-ion has a considerable influence on the reaction rate. Moreover, not one of the curves for the kinetic constant in Figure 7 approaches a constant value which is synonymous with a "non-constant" kinetic constant. Before discussing the results of the new kinetic approach, the reader is referred to Figure 8 where the activity coefficients of CO_2 and OH^- for the three systems of interest are depicted. It is easy to see that the CO_2 activity coefficients for the three different counter-ions differ from each other. Furthermore the course of the CO_2 activity coefficients resembles the trend of the kinetic constants depicted in Figure 7. The activity coefficients of the hydroxide ions diverge less pronounced from each other although the difference is still noteworthy especially for the potassium ion compared to the two other counter-ions sodium and lithium.

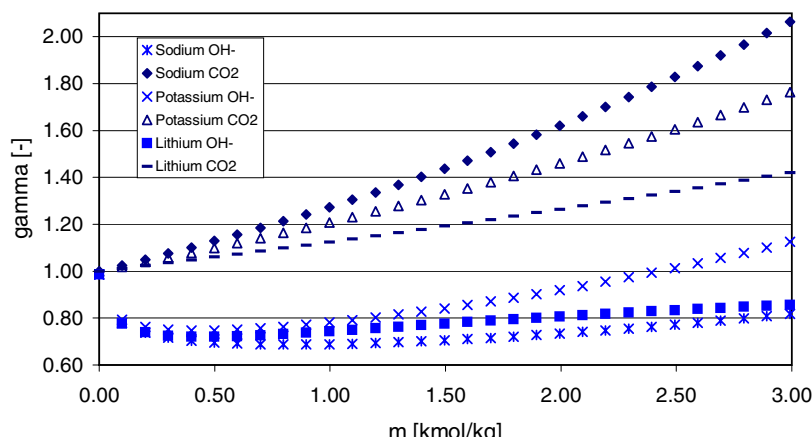


Figure 8. Dependence of the activity coefficients on molality

Applying these activity coefficients to normalize the three lumped kinetic constants of Pohorecki yields to the results illustrated in Figure 9. As can be seen from this Figure the dependence of the rate constant k_{OH^-} on the ionic strength diminishes considerably if normalized by the activity coefficients γ_{CO_2} and γ_{OH^-} . By dividing the ionic strength dependent "traditional" kinetic constant k_{OH^-} with the activity coefficients γ_{CO_2} and γ_{OH^-} , the spread of the resulting kinetic constant could be reduced remarkably in the new approach. The spread between the kinetic constants is especially reduced for the potassium and the sodium salt whereas the decrease is less pronounced for the lithium salt (see Figure 9).

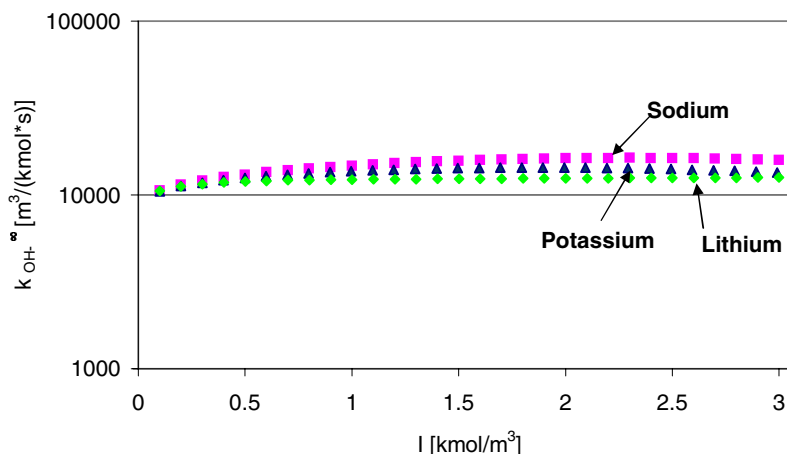


Figure 9. New kinetic approach incorporating activity coefficients

Moreover, it has been shown that by implementing activity coefficients in the kinetic expression (Eqn. 18) the kinetic rate constant stays at a virtually constant value except for the range below 1 kmol/m³ (Figure 9). In the region between 1 kmol/m³ and 3 kmol/m³ the kinetic constant varies by a maximum of 6 % for the potassium salt, by a maximum of 9 % for the sodium salt and by a maximum of 3 % for the lithium salt.

It is also worthwhile to mention that the absolute values of the reaction rate constant k_{OH^-} for the three different counter-ions are merging. Taking the value of the reaction rate constant for lithium at 3 mol/kg as a reference state, the reaction rate constant for potassium differs by 8 % from this value whereas the reaction rate constant for sodium differs by 25 % from this value. This is still a remarkable reduction compared to the deviations of 190 % for the potassium ion and 75 % for the sodium ion where all possible non-idealities are lumped in the reaction rate constant (see Figure 7).

Nevertheless the new activity based approach still exhibits a weakness in the regime below 1 kmol/m³ where the activity approach still shows a dependence of the kinetic constant on the ionic strength. One reason could be that Pohorecki and Moniuk (1988) excluded data below an ionic strength of 0.5 kmol/m³ to extrapolate the value for the rate constant at infinite dilution. Thus they omit experimental data to satisfy their fitting.

Unfortunately the experimental raw data are not presented by Pohorecki et al. which makes it impossible to reinterpret their experimental data. The same holds for all other papers except the one written by Nijssing et al. (1959), where experimental raw data are presented. As the kinetic data presented by this author are around 20 % lower versus the data of Pohorecki and Moniuk (1988) and Hikita and Asai (1976), and no other experimental raw data are available in literature, it has to be concluded that it is desirable to have additional experimental measurements to validate the findings presented in this paper.

6 CONCLUSION

In this study it has been shown that for the kinetics of the CO₂-OH⁻ reaction it is possible to account for liquid phase non-idealities by applying activity coefficients in the kinetic expression. Because the use of activity coefficients in kinetic expressions necessitates the application of a suitable equilibrium model, this method is more laborious than the use of traditional kinetic expressions that are typically based on the use of only concentrations.

Nevertheless, the use of activity coefficients in kinetic expressions seems especially useful for systems where the activity coefficients deviate substantially from one: in traditional kinetic expressions this non-ideal behavior would be lumped into the kinetic rate constant and in turn this would result in a concentration dependent reaction rate "constant". For the selected model system, the new approach seems to yield a near constant reaction rate constant over a wide concentration range, which is a clear benefit in comparison to

the traditional approach. In addition to this, the use of activity coefficients in kinetic expressions makes the description of thermodynamics and kinetics much more "compatible" compared to only using concentrations in kinetic expressions.

Therefore the application of the new methodology is thought to be very beneficial especially in processes where the "thermodynamics meet the kinetics". Hence it is anticipated that the new kinetic approach will firstly find its major application in the modeling of integrated processes like Reactive Distillation, Reactive Absorption and Reactive Extraction where both, thermodynamics and kinetics, are of essential importance and activity coefficients deviate substantially from ideal behavior.

ACKNOWLEDGEMENT

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NOMENCLATURE

| | |
|--------------|---|
| A_ϕ | Debye-Hueckel parameter, [-] |
| a | liquid phase activity, $[kmol/m^3]$ |
| $B_{CO_2,w}$ | mixed virial coefficient CO ₂ -water, $[cm^3/mol]$ |
| c | concentration, $[kmol/m^3]$ |
| C^ϕ | third virial coefficient in Pitzer's model, $[Pa]$ or $[bar]$ |
| D | relative dielectric constant of water, [-] |
| e | proton charge, $[C]$ |
| H | Henry's constant, $[Pa]$ or $[bar]$ |
| I | ionic strength, $[kmol/m^3]$ |
| k | Boltzmann's constant, $[J/K]$ |
| K^{EQ} | chemical equilibrium constant, [-] |
| k_{OH^-} | rate constant, $[m^3/(kmol\ s)]$ |
| m | molality, $[mol/kg]$ |
| M_i | molar mass, $[kg/mol]$ |
| n | mole of substance, $[mol]$ |
| N_A | Avogadro's number, [-] |
| p | pressure, $[MPa]$ |
| r | second order reaction rate, $[kmol/(m^3\ s)]$ |
| R | universal gas constant, $[J/mol/K]$ |
| T | temperature, $[K]$ |
| v | partial molar volume, $[cm^3/mol]$ |
| y | mole fraction in the gas phase, [-] |
| z | number of charges, [-] |

Greek symbols

| | |
|----------------|---|
| $\beta_{i,j}$ | second virial coefficient, $[cm^3/mol]$ |
| ϵ_0 | vacuum permittivity, $[C^2/N/m^2]$ |
| ϕ | fugacity, [-] |
| γ | activity coefficient, [-] |
| ν | stoichiometric coefficient, [-] |
| ρ | density, $[kg/m^3]$ |
| $\tau_{i,j,k}$ | ternary interaction parameter, [-] |

Subscripts and Superscripts

| | |
|----------|----------------------------------|
| EQ | equilibrium |
| i | component i |
| j | component j |
| k | component k |
| m | molality scale |
| s | saturated |
| v | component i |
| ∞ | at infinite dilution or infinite |
| θ | initial value |
| " | gas phase |
| * | normalized to infinite dilution |
| w | water |

A BRIEF OUTLINE OF PITZER'S MODEL

In Pitzer's model for the excess Gibbs energy of an aqueous, salt containing system the osmotic coefficient and the mean activity coefficients are represented by a virial expansion in terms of molalities Pitzer (1973). The Pitzer model has been applied successfully to numerous electrolyte systems. Beutier and Renon (1978) used a simplified form of Pitzer's model for the calculation of vapor-liquid equilibria in aqueous solutions of volatile weak electrolytes such as NH_3 , CO_2 and H_2S . Engel (1994) applied the multicomponent, extended Pitzer model to allow for the liquid phase non-idealities in aqueous solutions of 1:1 bicarbonate and formate salts with a common ion. For this system the equilibrium conversion and the solubility of the electrolyte mixture were predicted within 5 % error on the basis of the thermodynamic model used. Rumpf et al. (1998) applied Pitzer's model to correlate new data for the solubility of carbon dioxide in aqueous solutions of acetic acid. According to the authors the developed model for the description of simultaneous chemical and phase equilibria correlates the experimental data in the range of the experimental uncertainty.

For a summary of the Pitzer model and its modifications the reader is referred to Pitzer (1991) and Zemaitis et al. (1986). The latter monograph gives a very good overview of models used for calculating activity coefficients in electrolyte solutions.

Pitzer's equation for the excess Gibbs energy reads as follows (Pitzer, 1973) :

$$\frac{G^E}{R \cdot T \cdot n_w \cdot M_w} = f_1(I) + \sum_{i \neq w} \sum_{j \neq w} m_i m_j \cdot \left(\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} f_2(x) \right) + \sum_{i \neq w} \sum_{j \neq w} \sum_{k \neq w} m_i \cdot m_j \cdot m_k \cdot \tau_{i,j,k} \quad (20)$$

whereas $\beta_{i,j}^{(0)}$ and $\beta_{i,j}^{(1)}$ are binary and $\tau_{i,j,k}$ are ternary interaction parameters, respectively. The function $f_1(I)$ is a modified Debye-Hueckel term

$$f_1(I) = -A_\phi \frac{4I}{b} \ln \left(1 + \sqrt{I} \right) \quad (21)$$

wherein the ionic strength I is defined as:

$$I = 0.5 \cdot \sum_i m_i z_i^2 \quad (22)$$

and $b = 1.2 (kg/mol)^{0.5}$ is a fixed parameter. In equation 21 A_ϕ is the Debye-Hueckel parameter for the osmotic coefficient which is defined as

$$A_\phi = \frac{1}{3} \left(2 \pi N_A \frac{\rho_w}{1000} \right)^{0.5} \left(\frac{e^2}{4 \pi \epsilon_0 D k T} \right)^{1.5} \quad (23)$$

The function $f_2(x)$ is defined as

$$f_2(x) = \frac{2}{x^2} (1 - (1 + x) e^{-x}) \quad (24)$$

with $x = \alpha \sqrt{I}$. For the salts considered in this study, α equals $1.2 (kg/mol)^{0.5}$.

The activity coefficients of the dissolved species i can be obtained by differentiation of equation 20:

$$\begin{aligned} \ln \gamma_i^* = & -A_\phi z_i^2 \left(\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b} \ln(1 + b\sqrt{I}) \right) + 2 \sum_{j \neq w} m_j \left(\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} f_2(x) \right) \\ & - z_i^2 \sum_{j \neq w} \sum_{k \neq w} m_j m_k \beta_{j,k}^{(1)} f_3(x) + 3 \sum_{j \neq w} \sum_{k \neq w} m_j m_k \tau_{i,j,k} \end{aligned} \quad (25)$$

where f_3 is defined as

$$f_3 = \frac{1}{I x^2} (1 - (1 + x + 0.5 x^2) e^{-x}) \quad (26)$$

The activity of water follows from the Gibbs-Duhem equation

$$\begin{aligned} \ln a_w = & M_w \left(2 A_\phi \frac{I^{1.5}}{I + b\sqrt{I}} - \sum_{i \neq w} \sum_{j \neq w} m_i m_j \left(\beta_{i,j}^{(0)} + \beta_{i,j}^{(1)} e^{-x} \right) \right) \\ & - M_w \left(2 \sum_{i \neq w} \sum_{j \neq w} \sum_{k \neq w} m_i m_j m_k \tau_{i,j,k} + \sum_{i \neq w} m_i \right) \end{aligned} \quad (27)$$

For systems containing a single salt of the form $M_{\nu+} X_{\nu-}$, the binary and ternary parameters involving two or more species of the same sign of charge are typically neglected. The ternary parameters $\tau_{M,X,X}$ and $\tau_{M,M,X}$ are usually reported as third virial coefficients C^ϕ for the osmotic coefficient.

To circumvent the rewriting of equations 25 and 27 in terms of C^ϕ , the ternary parameter $\tau_{M,X,X}$ has been set to zero and the parameters $\tau_{M,M,X}$ have been calculated from numbers reported for C^ϕ :

$$\begin{aligned} 1:1 \quad \text{salt} \quad \tau_{M,M,X} &= \frac{1}{3} C^\phi \\ 2:1 \quad \text{salt} \quad \tau_{M,M,X} &= \frac{\sqrt{2}}{6} C^\phi \end{aligned}$$

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